

# Cyanoacrylate Adhesives: A Critical Review

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**Abstract:** Cyanoacrylates have found their forte as an easy to use, fast setting, strong adhesives for a wide variety of applications since 1950. Even though the serendipitous discovery of cyanoacrylate adhesives was at Eastman Kodak Labs, the journey of a cyanoacrylate adhesive towards most widely used adhesive for a variety of application areas has been a result of decades of innovation and hard work by many. This review particularly focuses on the synthesis, chemistry, processing and applications of cyanoacrylate adhesives from a historical perspective to recent advances. Special emphasis is given to industrial, consumer, medical, and forensics applications of cyanoacrylate adhesives. Recent advances in cyanoacrylate adhesives, especially, structuring cyanoacrylate adhesives in the form of nanofibers by using different techniques, and their applications are discussed in detail as well.

**Keywords:** Cyanoacrylate esters, knoevenagel reaction, tissue adhesive, cyanoacrylate fuming, nanofibers, cyanoacrylate fibers

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## 1 Introduction

Cyanoacrylate adhesives are one of the most versatile and widely used adhesives in the world for a variety of applications. Like every great invention, the adhesive use of cyanoacrylates was discovered accidentally by scientists at Eastman Kodak Company in 1951, while doing a refractive index measurement on ethyl 2-cyanoacrylate samples made for heat-resistant jet plane canopy application. Ethyl 2-cyanoacrylate sample stuck the prisms of the refractometer. Even though the scientists initially panicked, they quickly recognized the value of this material as adhesive [1–4]. Eastman commercialized the first cyanoacrylate adhesive as Eastman 910® in 1958 [4]. Developments followed and several other producers including Loctite, Sumitomo, and Henkel emerged in the market with further optimized cyanoacrylate solutions in the 60s through 80s. The versatility of this adhesive chemistry to join a variety of substrates, quick bonding, high bond strength and the simplicity in application made cyanoacrylate adhesives one of most popular adhesives used around the world. Cyanoacrylates show excellent

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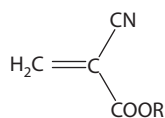
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adhesion to a variety of materials, including plastics, rubber, metals, ceramics, wood, glass, paper, cloth, cement and tissue [3, 5–8]. Dr. Harry Coover, who led the team of scientists who invented cyanoacrylate adhesives at Eastman, was honored with the National Medal of Technology and Innovation in 2010, the highest honor given to scientists by the United States government for their long lasting contribution to the society through science and innovation [9].

Even though Eastman Kodak pioneered the art of engineering cyanoacrylates as adhesives in the 50s, the cyanoacrylate chemistry to make clear glass-like resins had been reported in the 40s [10, 11]. Journey towards the commercial success of cyanoacrylate adhesives has been a challenging one, especially regarding their production and storage, due to their fast setting characteristics at room temperature. The monomeric  $\alpha$ -cyanoacrylate polymerizes very fast in the presence of weak bases without heat or catalyst at room temperature. Chemical nature and electronic configuration of  $\alpha$ -cyanoacrylates are responsible for the processing and storage issues (without premature polymerization) [1]. However, this rapid polymerization characteristic of the liquid  $\alpha$ -cyanoacrylate monomer in the presence of weak bases makes it a great fast setting adhesive as well [1–6].

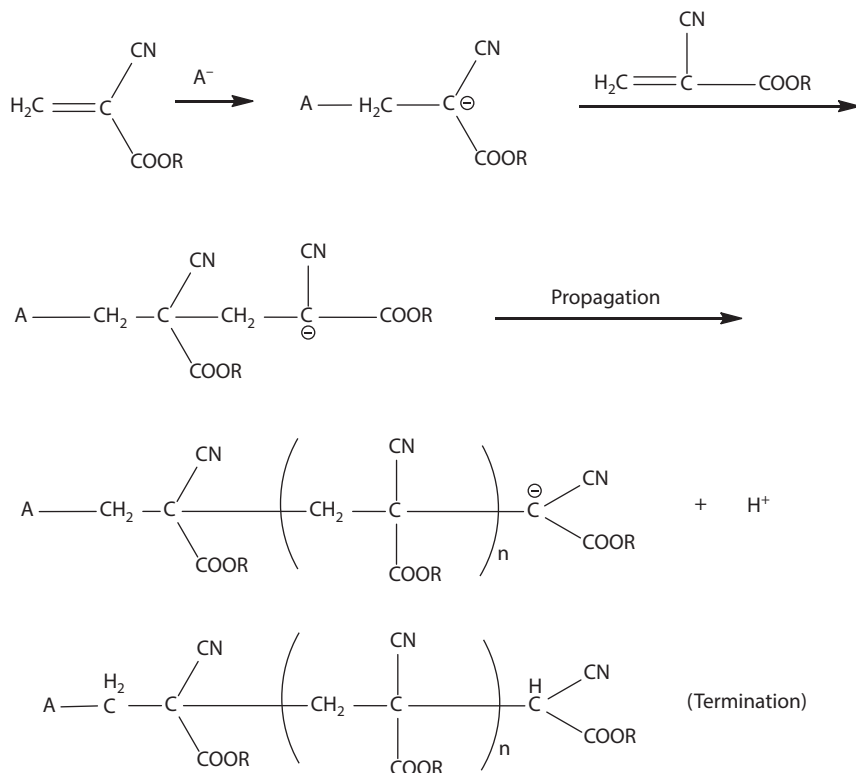
## 2 Synthesis and Processing

Cyanoacrylate monomers can be generally characterized as acrylate backbone with two electronegative groups as shown below. These electron withdrawing groups can undergo anionic polymerization in the presence of bases to form a glass-like polymer [8, 12, 13].



Not all  $\alpha$ -cyanoacrylates perform as adhesives. Typically alkyl 2-cyanoacrylates are preferred for adhesives applications [1, 8, 12–19]. The presence of very effective electron withdrawing cyano (CN) and carboxyl ester (COOR) functionalities differentiates the alkyl 2-cyanoacrylates from other  $\alpha$ -cyanoacrylates. These two strong electronegative (cyano and carboxyl) groups help undergo rapid anionic polymerization with weak bases such as water, alcohols, etc., and results in a high molecular weight polymer through the carbanion as shown in Scheme 1 [1, 5, 8, 20]. The excellent stability of the carbanion formed, stabilized by the electron withdrawing cyano (-CN) and ester (-COOR) groups is the fundamental reason for rapid setting characteristics of these materials.

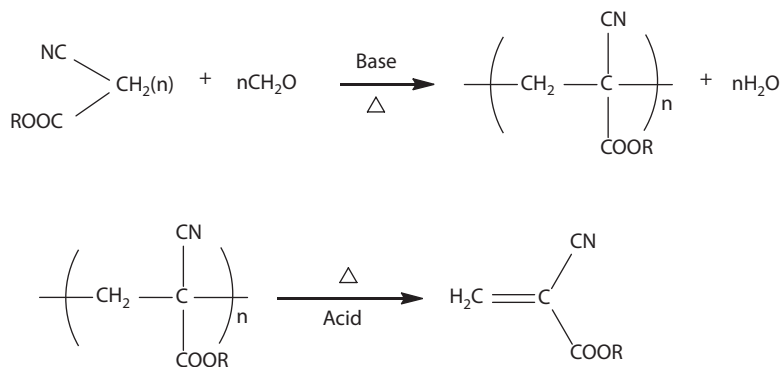
Alkyl  $\alpha$ -cyanoacrylate monomers were commercially produced by condensation-depolymerization method, known as the Knoevenagel reaction. First, an alkyl  $\alpha$ -cyanoacrylate polymer is produced through condensation reaction of alkyl cyanoacetate with formaldehyde in the presence of a base (e.g. amine). The alkyl  $\alpha$ -cyanoacrylate monomer cannot be isolated during this reaction because base



**Scheme 1** Anionic polymerization of alkyl 2-cyanoacrylate.

initiates cyanoacrylate polymerization. The base catalyst is typically neutralized at the end of polymerization by addition of small amounts of acidic compound such as phosphoric anhydride. This polymer was then depolymerized at higher temperatures (140–260 °C) under acidic conditions (e.g. phosphoric anhydride) to obtain the alkyl 2-cyanoacrylate monomer, as shown in Scheme 2 [1, 5, 14–21].

Alkyl  $\alpha$ -cyanoacrylate monomer must be well stabilized during manufacturing, storage and transport to prevent polymerization before the intended use, due to its inherent reactivity characteristics in the presence of free radicals and bases. Widely known cyanoacrylate monomer stabilizers can be divided into two main categories: anionic inhibitors and free radical inhibitors. Free radical inhibitors include hydroquinone, catechol, hindered phenols and their derivatives. Anionic inhibitors include Lewis or protonic acids. Acidic gases like hydrogen fluoride, boron trifluoride, nitric oxide, sulfur dioxide, sulfur trioxide, etc. are effectively used during manufacturing process to prevent premature polymerization (in distillation columns, pipes, head-space, etc.), since these gases can stabilize the cyanoacrylate monomer in both liquid and gaseous phases. Other acidic compounds



**Scheme 2** Condensation-depolymerization reaction to produce alkyl 2-cyanoacrylate.

such as picric acid, maleic acid, maleic anhydride, metaphosphoric acid, phosphorous pentoxide, antimony oxide, ferric chloride, alkyl sulfates, alkyl sulfones, mercaptans, alkyl sulfides, different silane treated silica, different sulfur containing compounds, oxonium and phosphonium compounds; and organic-inorganic acids with pKa values from -12 to 7 in combination with acid gas stabilizers are also used. Type, amount and strength of an acidic stabilizer should be carefully considered during the selection of right anionic inhibitor, since stabilizers can also influence the setting characteristics of the adhesive during application, causing insufficient bond strength [2, 8, 10, 11, 14–29].

Several different alkyl substituted cyanoacrylate esters have been manufactured using the normal condensation and depolymerization method. Physical properties of a variety of alkyl substituted (methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, and allyl) cyanoacrylate monomers were studied and reported by several scientists including Leonard *et al.* [5] and Coover and McIntire [8]. Klemarczyk [28] correlated the physical properties with major end use markets and applications. Typical reported physical properties for alkyl  $\alpha$ -cyanoacrylate monomers and some of the respective markets/applications are given in Table 1. Considerable process development efforts followed (including catalyst optimization, *in-situ* impurities removal, enhanced heat transfer solvents, azeotropic distillation, etc.) to optimize the Knoevenagel reaction since 1950s through 1980s, mainly to increase the yield, purity and stabilization of the alkyl  $\alpha$ -cyanoacrylate monomers [10, 11, 14–27].

Other than the above-mentioned hydrocarbon-based alkyl 2-cyanoacrylates, several specialty (polar and crosslinking) mono and difunctional cyanoacrylate esters were also synthesized through condensation-depolymerization reaction method for use as adhesives. These include Allyl 2-cyanoacrylate, Ethylene glycol di-2-cyanoacrylate, Neopentyl glycol di-2-cyanoacrylate, Dicyanoacrylate of poly (ethylene glycol) and thiocycanoacrylates [29, 30]. Synthesis of a difunctional

Table 1 Physical properties and uses of different alkyl substituted cyanoacrylate esters [5, 8, 28].

| Type of alkyl group | Molecular weight [5] | Density [5], (20 °C), g/cm <sup>3</sup> | Boiling point [5], °C/mm.Hg | Brookfield viscosity [8], (25 °C), cP | Refractive index [5], (20 °C) | Surface tension [5], (mN/m) | Markets/ applications [28] |
|---------------------|----------------------|-----------------------------------------|-----------------------------|---------------------------------------|-------------------------------|-----------------------------|----------------------------|
| Methyl              | 111                  | 1.10                                    | 55/4                        | 2.2                                   | 1.4459                        | 37.41                       | General purpose            |
| Ethyl               | 125                  | 1.04                                    | 60/3                        | 1.86                                  | 1.4391                        | 34.32                       |                            |
| Propyl              | 139                  | 1.00                                    | 80/6                        | 1.95                                  | 1.4408                        | 32.8                        | Rubber Bonding             |
| Butyl               | 153                  | 0.99                                    | 68/1.8                      | 2.07                                  | 1.4424                        | 31.11                       | Medical, Veterinary        |
| Amyl/Pentyl         | 167                  | 0.97                                    | 113/5.4                     | 3.32                                  | 1.444                         | 30.25                       | –                          |
| Hexyl               | 181                  | 0.96                                    | 90/1.6                      | 3.66                                  | 1.4458                        | 29.98                       | –                          |
| Heptyl              | 195                  | 0.94                                    | 125/1.2                     | –                                     | 1.4466                        | 30.28                       | –                          |
| Octyl               | 209                  | 0.93                                    | 117/1.8                     | 3.92                                  | 1.4489                        | 29.18                       | Industrial assembly        |
| Allyl               | 137                  | 1.07                                    | 74/4.2                      | 2.0                                   | 1.4586                        | 35.38                       | Crosslinking applications  |



**Table 2** Effect of alkyl group on polymerization reaction rate at 50 °C.

|                      |                                               |
|----------------------|-----------------------------------------------|
| Homogeneous system   | Isopropyl < Isobutyl < Butyl < Ethyl < Methyl |
| Heterogeneous system | Isopropyl < Isobutyl < Ethyl < Butyl < Methyl |

cyanoacrylate monomer through a reverse Diels-Alder reaction of a dicyanoacrylate precursor was also reported for adhesives use as well [31]. The type of alkyl group and type of anionic (water, alcohol, etc.) or free radical initiator can affect the kinetics of condensation reaction between formaldehyde and alkyl cyanoacetate. Successful polymerization using free radical initiators necessitated the exclusion of weak bases such as moisture, alcohols, etc. from the reaction process to avoid anionic polymerization [19, 32]. Effect of alkyl groups on polymerization reaction rates at 50 °C, in a homogeneous system and a heterogeneous system is shown in Table 2 [33].

The degradation/depolymerization (at 150 °C–230 °C, under N<sub>2</sub>) rates of polymer into respective alkyl  $\alpha$ -cyanoacrylate monomer follow the same order as homogeneous system [33]. From in-vitro kinetic studies on an alkyl 2-cyanoacrylate based tissue adhesive under homogeneous and heterogeneous conditions, it was concluded that cyanoacrylate polymer degraded by hydrolytic scission of the polymer chain, and the rates obtained with the methyl to butyl derivative followed the same order as homogeneous system (see Table 2) [5].

### 3 Applications

Alkyl 2-cyanoacrylate monomers are used in a wide range of applications, including industrial, consumer medical and forensics, due to their instant reactivity to form strong bonds with a variety of surfaces (both low and high energy surfaces) in the presence of moisture. However, in most cases alkyl 2-cyanoacrylates are formulated with different additives such as fillers, thickeners, plasticizers, and stabilizers for applicability and optimum performance in intended uses [8, 12, 20, 28, 33].

#### 3.1 Industrial and Consumer

Alkyl 2-cyanoacrylate adhesives were an instant success since their introduction in late 1950s for a wide variety of industrial applications, including automotive (bonding interior and exterior parts/modules), electrical and electronics (bonding parts of switches, loud speaker parts, printed circuit boards, parts of control knobs, etc.), machinery (bonding dissimilar substrates such as metals to plastics, plastics to rubber, metals to rubber, etc.) and many others. The main drivers for the instant adaption of cyanoacrylate adhesives into industrial sector were simplicity in application that can be automated very easily, instant bonding/high rate of cure directly impacting line speeds, ease of bonding a variety of different substrates, and all of these translating directly into lower production costs [8, 20, 28, 33–35].

Cyanoacrylate adhesives were introduced into the consumer market (in different package types) in 1973, and have been available with different names including Super Glue™, Crazy Glue™, PermaBond™, etc. [33]. It is impossible to cover all the applications, so a general overview with respect to cyanoacrylate chemistries and bonding technologies in industrial and consumer segments is presented.

Typically, cyanoacrylate adhesives are one-component systems that do not require premixing, shaking or heat/energy to cure. They are applied as drops (normally 1 drop/6.5 cm<sup>2</sup>) onto the substrate surface to be bonded. The fast setting of these adhesives occurs due to presence of the adsorbed moisture on almost all surfaces (at room temperature) resulting in very high bond strength [8, 33–37]. Several studies have been published to understand the effect of bonding efficiency (bonding time and strength) on different substrates. Coover and McIntire [8] published considerable data on the bonding efficiency on a variety of different substrate combinations, and observed that bonds formed on smooth-hard surfaces set faster than on porous-rough surfaces. Comparisons of bonding efficiency on different substrates by simple alkyl 2-cyanoacrylate esters are given in Table 3.

Simple alkyl 2-cyanoacrylate esters (especially lower alkyl esters) are water-thin, free-flowing materials resulting in clear, hard/brittle joints with low impact characteristics. Lower viscosity formulations bond 2–5 times faster than higher viscosity formulations, and can have a significant impact on gap filling properties resulting in different bond strength flexibilities and impact properties [33, 36]. Bond strength (steel/steel tensile shear strength) depends on the number of carbon atoms in the carboxyl ester group, especially for the simple alkyl 2-cyanoacrylate esters as shown below [34].

|          |            |           |         |           |           |
|----------|------------|-----------|---------|-----------|-----------|
| Methyl > | Ethyl >    | Propyl >  | Butyl > | Hexyl >   | Heptyl    |
| (18 MPa) | (15.6 MPa) | (9.3 MPa) | (8 MPa) | (3.1 MPa) | (0.9 MPa) |

Bulk properties (melting point, softening point, refractive index, dielectric properties, etc.) and bond properties (set time, bond strength, etc. to different substrates) of simple alkyl 2-cyanoacrylate adhesives and common commercially available cyanoacrylate adhesives were also reported in detail by Coover and coworkers [8, 20, 36]. Simple alkyl 2-cyanoacrylate esters show low heat resistance or loss of bond strength at elevated temperatures (typically around 80 °C) resulting in bonded joint failures. This is due to the low glass transition temperature (*T<sub>g</sub>*) of the polymer, and can also be correlated to the low onset temperature of thermal degradation [8, 33, 37]. Heat resistance can be achieved through several different ways. Allyl 2-cyanoacrylate shows higher heat resistance when cross-linked through the allyl double bond. Allylic double bond enables the secondary bonding/crosslinking reaction between the adjacent polymer chains, in the presence of peroxide or with just heat [34]. Heat resistance characteristics of methyl cyanoacrylate and allyl cyanoacrylate on a steel-steel lap shear joint at different temperatures are given in Table 4 [34].

**Table 3** Bonding efficiency on different substrates [8].

| Substrates                                | Bond strength /[Bond setting time, seconds] |
|-------------------------------------------|---------------------------------------------|
| Aluminum – Aluminum                       | Intermediate / [ $\leq 180$ ]               |
| Steel – Steel                             | Strong / [ $\leq 180$ ]                     |
| Steel – Neoprene                          | Strong / [ $< 60$ ]                         |
| Polyethylene – Polyethylene               | Intermediate / [ $\leq 180$ ]               |
| Poly (ethylene terephthalate) (PET) – PET | Intermediate / [ $< 60$ ]                   |
| Nylon – Nylon                             | Intermediate / [ $< 60$ ]                   |
| Glass – Glass                             | Strong / [ $< 60$ ]                         |
| Glass – Rubber                            | Strong / [ $< 60$ ]                         |
| Glass – Textile (Felt)                    | Strong / [ $< 60$ ]                         |
| Glass – Steel                             | Strong / [ $\leq 180$ ]                     |
| Wood – Wood (Maple)                       | Strong / [ $> 180$ ]                        |
| Metal – Leather                           | Strong / [ $\leq 180$ ]                     |
| Metal – Rubber                            | Strong / [ $< 60$ ]                         |
| Metal – Textile (Felt)                    | Strong / [ $< 60$ ]                         |
| Rubber – Rubber                           | Strong / [ $< 60$ ]                         |
| Rubber – Cardboard                        | Strong / [ $< 60$ ]                         |
| Porcelain – Porcelain                     | Strong / [ $< 60$ ]                         |

**Table 4** Heat resistance/high temperature bond strength comparison of allyl and methyl cyanoacrylates [34].

| Temperature (°C)                                     | 25    | 100   | 120  | 150   | 250   |
|------------------------------------------------------|-------|-------|------|-------|-------|
| Steel/Steel Tensile Shear Strength (ASTM D1002), MPa |       |       |      |       |       |
| Methyl Cyanoacrylate                                 | 24.82 | 1.72  | 0    | 0     | 0     |
| Allyl Cyanoacrylate                                  | 20.68 | 26.89 | 6.21 | 10.34 | 11.72 |

As can be seen in Table 4, the strength of the methyl cyanoacrylate is drastically reduced at 100 °C and completely lost above 120 °C. Allyl cyanoacrylate bond strength is also reduced at 120 °C due to the loss of strength by intermolecular association of cyanoacrylate backbone and the only contribution remaining is from the crosslinked allylic chains. The slightly higher bond strength for allylic cyanoacrylate at 150 °C and 250 °C is mainly due to the higher crosslinking of allylic groups at elevated temperatures [34]. Further improvement in heat resistance was achieved through improved crosslinking by introducing different

alkenyl and alkynyl groups (triple and double bonds) into the cyanoacrylate ester group with different chain lengths (number of carbon atoms) [38]. Copolymers of alkyl 2-cyanoacrylates with fluoro-compounds [39] and cyanuric chloride [33] have been shown to improve heat resistance/high temperature bond strength up to 30%.

Industrial applications can have viscosities ranging from 2cP to 3000cP, depending on the handling and application of the adhesive. High viscosity cyanoacrylate adhesives are ideal candidates for porous substrates and gap containing joints [33, 37]. Viscosity, rheology, flexibility and impact characteristics of alkyl 2-cyanoacrylates are typically modified by formulating with different thickener polymers and copolymers (such as polymethacrylates, polyacrylates, cellulose nitrate, cellulose acetate, cellulose butyrate, acrylonitrile-butadiene-styrene, ethylene methacrylate, etc.), plasticizers (such as phthalates, adipates, sebacates, succinates etc.) and even using some specialty fillers (such as silane treated fumed silica) [3, 7, 8, 19, 27, 34, 36, 37, 40–42]. Using acidic treated carbon and metal powders as fillers, an electro-conductive cyanoacrylate adhesive composition was developed for electronic applications [37].

Bonding cyanoacrylate adhesives to acidic surfaces (such as wood, paper, textiles, etc.) is challenging (long set time, see Table 3). Improved bonding set times and high bond strength to acidic surfaces is achieved through two techniques. The first technique involves proper surface cleaning/pretreatment, and the second technique involves formulating with different additives. Solvents such as acetone and naphtha are good cleaning agents to remove contaminants or slightly acidic materials; while for highly acidic substrates, treating the surface with a surfactant solution or treating with methylol (etherified) derivatives of urea or melamine has been shown to be effective [8, 33, 36]. Formulating cyanoacrylates with additives such as a weakly basic ionic compound ( $\text{CF}_3\text{SO}_3\text{K}$ ) [33], or sequestering agents such as crown ethers, calixarenes, polyalkylene ethers has been shown to accelerate cure, reduce set times and increase bond strength of cyanoacrylate adhesives on acidic surfaces [43–47].

As can be seen in Table 3, achieving sufficient bond strength on low surface energy substrates (such as polyethylene, polyesters, nylon etc.) using cyanoacrylate adhesives has been challenging as well. Improved bond strength to polyolefin substrates using cyanoacrylate adhesives is achieved by priming the substrate surface using dilute solutions of primers (typically activators/initiators such as diazabicyclo and triazabicyclo compounds, trialkyl and tetraalkyl ammonium salts, phosphines, organometallic compounds, tertiary aliphatic/aromatic amines, etc.) followed by applying the adhesive after solvent evaporation [48–51]. A comparison of bond strengths using a standard industrial grade cyanoacrylate, for bonding a primed and a non-primed polyethylene (PE) and polypropylene (PP) substrates was reported by Repensek [34] and is shown in Table 5.

A solvent-free/primer-free way to achieve sufficient bond strength for polyolefin substrates, including bonding intricate designs for high speed assembly

**Table 5** Bond strengths of a standard industrial grade cyanoacrylate adhesive on primed and non-primed polyolefin substrates [34].

| Lap shear strength at room temperature, MPa | PE/PE  |            | PP/PP  |            |
|---------------------------------------------|--------|------------|--------|------------|
|                                             | Primed | Non-primed | Primed | Non-primed |
| After 15 minutes                            | 0.62   | 0.34       | 1.28   | 0.36       |
| After 24 hours                              | 0.74   | 0.34       | 1.38   | 0.36       |

processes, was addressed by light curing cyanoacrylate adhesives [52–54]. Light curing cyanoacrylate adhesives are based on ethyl cyanoacrylate monomer and can be cured using an ultraviolet (UV) or visible light sources via an anionic cure mechanism (like typical cyanoacrylates) [53]. Light curing cyanoacrylates are mainly used in medical device manufacturing applications including needle bonding (to bond stainless steel cannula to colored polypropylene hub in a syringe assembly) and tubeset bonding (bonding a plasticized poly (vinyl chloride) tube to a polycarbonate stem in medical applications) [54]. Main advantages of light curing cyanoacrylates compared to standard moisture cured cyanoacrylates include [52–54],

- In-depth cure in depths exceeding 6.35 mm can be obtained using light cure compared to maximum cure depth of about 0.254 mm for standard surface initiated cyanoacrylates
- Effective curing of exposed adhesive fillet using light curing cyanoacrylates, thus preventing blooming (when using standard moisture cure cyanoacrylate)

Typical bond strengths of low and high viscosity cyanoacrylate adhesives on different substrates are given in Table 6 [52, 54].

### 3.2 Medical

Cyanoacrylate adhesives have been a prime candidate for medical applications including dentistry, especially as tissue adhesives and sealing materials, since their commercial introduction in 1958, due to their fast setting characteristics in wet environment to form strong flexible bonds. As for industrial adhesives, majority of the cyanoacrylate based medical adhesives are alkyl 2-cyanoacrylate monomers formulated with different modifiers such as plasticizers, thickeners and stabilizers [5, 55, 56]. Since the first commercial introduction of Eastman 910® cyanoacrylate adhesive, this methyl 2-cyanoacrylate monomer based adhesive was also evaluated for patching, anastomosis and shunting of small arteries and

Table 6 Bond strengths of light curing cyanoacrylate adhesives on different substrates (ASTM D4501), MPa [52, 54].

| Substrate                                   | ABS*  | Acrylic | Aluminum<br>(etched) | Neoprene | Phenolic | Polycarbonate<br>(PC) | Poly (vinyl<br>chloride)<br>(PVC) | Steel (grit<br>blasted) |
|---------------------------------------------|-------|---------|----------------------|----------|----------|-----------------------|-----------------------------------|-------------------------|
| Low viscosity<br>cyanoacrylate<br>(~20cP)   | 34.40 | 13.24   | 17.58                | 0.76     | 7.17     | 28.68                 | 33.09                             | 17.86                   |
| High viscosity<br>cyanoacrylate<br>(~900cP) | 35.65 | 14.13   | 17.93                | 0.79     | 1.31     | 14.13                 | 32.68                             | 22.48                   |

\*Acrylonitrile butadiene styrene.



veins in dogs [57]. These experiments in 1960s initiated a series of attempts to use cyanoacrylate adhesives in surgery. However, medical evaluation of methyl 2-cyanoacrylate monomer and polymer as a tissue adhesive showed good adhesion, but found to cause acute inflammatory responses in tissues [5, 6]. Interestingly, for the butyl and higher alkyl 2-cyanoacrylate derivatives toxicity appears to be well tolerated by tissues [5]. The formation of toxic degraded products of the poly (alkyl 2-cyanoacrylate) decreases with increase in length of alkyl side chain and molecular weight of polymer [5, 58]. By 1971 there were almost 20 different programs in experimental and clinical evaluation stage using different alkyl substituted  $\alpha$ -cyanoacrylate adhesives in ocular surgery applications alone [57]. Only butyl cyanoacrylates, heptyl cyanoacrylates, octyl cyanoacrylates and ethoxyethyl cyanoacrylates based chemistries have progressed and commercialized for dental, medical and veterinarian use, mainly due to their [5, 6, 58, 59],

- Better ability to wet and spread on living tissue than their lower homologues.
- Lower heat generation during polymerization, which helps avoid necrosis of tissues.
- Better mechanical properties (especially flexibility) and cosmetic results.
- Improved toxicity - Degradation products can be metabolized and removed from the body.

In the United States (US), Food and Drug Administration (FDA) has approved only two different cyanoacrylate chemistries (n-butyl 2-cyanoacrylate and 2-octyl cyanoacrylate) so far and most of these are for external clinical use. Interestingly, internal use is not prohibited in other countries and the clinical trials are permitted by US-FDA. There has been a lot of reported literature and reviews [55–66] on internal medical use over the past several years. All these reviews have described the clinical studies in detail using cyanoacrylate adhesives for internal and external use including applications for topical skin additives, for endoscopic therapy of peptic ulcer bleeding, for colorectal variceal bleeding, for gastric varices, for corneal cataract incisions, for tissue reconstruction (nerve tissue, vascular tissue, etc.), peripheral embolization, for dermal lesions, for bonding bone and cartilage, etc. However, US-FDA has approved cyanoacrylate adhesives only for certain surgical applications (such as topical wound closure application and neurological embolization) [59], dental applications (such as dental cements, and orthodontic brackets) [56, 58] and veterinarian applications [59]. A list of US-FDA approved cyanoacrylate based medical adhesives, and their chemistry and commercial name is given in Table 7 [58, 59].

Even though n-butyl-2-cyanoacrylate is fast setting and forms uniform non-wrinkling films as tissue adhesives, it is relatively brittle and can fracture when used in long incisions. This can be overcome by use of 2-octyl-cyanoacrylate, which provides more flexibility and almost 3-times bond strength [58, 59]. Hence, the blend of butyl and octyl cyanoacrylates seems to provide a good balance of



**Table 7** US-FDA approved cyanoacrylate based medical adhesives [58, 59].

| Commercial name                                  | Cyanoacrylate chemistry         | Typical use                                                           |
|--------------------------------------------------|---------------------------------|-----------------------------------------------------------------------|
| Trufill®                                         | n-Butyl-2-cyanoacrylate         | Neurological embolization, Wound closure                              |
| Indermil®                                        | n-Butyl-2-cyanoacrylate         | Wound closure, Tissue adhesive. Microbial barrier                     |
| Dermabond®                                       | 2-Octyl-cyanoacrylate           | Wound closure, Tissue adhesive. Microbial barrier. High bond strength |
| PeriAcryl® (only premarket approval from US-FDA) | Butyl/Octyl cyanoacrylate blend | Dental cement - Oral cavity and periodontal dressing                  |

flexibility and bond strength coupled with fast setting characteristics. Primarily cyanoacrylate medical adhesives are packaged in high density polyethylene packages, since it provides necessary shelf-life up to 2-years (at ambient or refrigerated conditions) [59].

Toxicity of medical adhesives has been a major field of study since 1960s [5, 6, 67]. The cytotoxicity (effect on cells), hemolysis (effect on blood and its constituents), chlorosis (formation of white particles due to evaporation of liquid monomer without being polymerized) [34] etc., and overall systemic effects of cyanoacrylate adhesives have been evaluated using USP Class VI standard and ISO-10993 standard for biocompatibility [59, 67]. Cyanoacrylates should be handled only using appropriate personal protective equipment with proper ventilation, since cyanoacrylate is a powerful adhesive (rapid exothermic polymerization), and exposure to large quantities has been shown to cause irritation of eye, nose and throat [36, 56, 67, 68]. Additionally, cyanoacrylates should only be handled away from open flames, sparks and high heat, since both cyanoacrylate polymer and monomer support combustion [33, 36].

### 3.3 Forensics

For several decades, cyanoacrylate adhesives have been used as a forensic tool for latent fingerprinting by several investigation agencies around the world, through a technique known as cyanoacrylate fuming [69, 70]. Cyanoacrylate fuming is mainly the vapor phase anionic polymerization of a cyanoacrylate monomer, in which a cyanoacrylate monomer ester is vaporized under controlled conditions in a fuming chamber, and exposed to latent fingerprints. Fingerprint residue initiates the polymerization reaction of the cyanoacrylate monomer vapor, forming white polymer solids, and exposes the ridges and definitions of the fingerprints [69–74].

Reaction mechanism involving methyl cyanoacrylate [73] and ethyl cyanoacrylate [74] revealed that the carboxyl moiety is the primary initiator of the polymerization process and the water cannot be the primary initiator in the cyanoacrylate fuming forensic technique [70, 72, 74]. The fingerprint response also depends on several factors (viscosity, amount fumed, film thickness, etc.) of the adhesive fuming [70, 72, 73].

### 3.4 Recent Advances in Cyanoacrylate Adhesives

In recent years, there has been considerable activity and interest in structuring cyanoacrylate adhesives in the form of nanofibers, produced using different techniques, for a wide variety of applications including tissue engineering, biomedical devices, self-cleaning polymer surfaces, and filtration [75–79]. Pennsylvania State University scientists have studied the rapid polymerization mechanism of ethyl 2-cyanoacrylate in controlled conditions using the fuming chamber that allows the growth of cyanoacrylate polymer on a silicon wafer at different relative humidities. They saw formation of large quantities of high aspect ratio nanofibers of ethyl 2-cyanoacrylate polymer on the crest of the fingerprint, especially at high relative humidity. These fibers seem to deposit only in areas where initiator was present with a fiber diameter ranging from 100nm to 400nm [75]. Reaction conditions and initiator type influence the morphology of these cyanoacrylate fibers made using this facile, template-less vapor phase catalytic route [75]. Nanofiber formation of ethyl 2-cyanoacrylate polymer on different silane treated glass surfaces through the vapor phase polymerization has been shown to occur at lower relative humidities [76]. Several other techniques for producing cyanoacrylate nanofibers have been successfully demonstrated recently. Ecofriendly, solvent-less electrospinning of ultrathin polycyanoacrylate fibers was reported by Liu *et al.* [77], in which a spinning solution of ethyl 2-cyanoacrylate monomer and poly (methyl methacrylate) was polymerized into nanofiber structures utilizing the rapid polymerization of cyanoacrylate monomer in the presence of moisture. Jiang *et al.* [78] reported medical glue for rapid hemostasis in liver resection using n-octyl-2-cyanoacrylate ultrathin fibers onto a wound surface. These nanofibers were produced using an airflow-directed in situ electrospinning method to obtain an electro-spun octyl cyanoacrylate fibrous membrane with high strength, flexibility and integrity [78].

However, one of the biggest challenges for the synthesis of cyanoacrylates nanofibers has been the higher reactivity and rapid polymerization of alkyl 2-cyanoacrylate monomers in the presence of weak bases and free radicals, limiting the nanofibers to 1D nanostructure. Producing large quantities of long cyanoacrylate fibers with well-defined nanostructure morphologies has been challenging. Very recently (September 2015), electrospinning of highly uniform and long well-defined fibers of ethyl 2-cyanoacrylate polymer was achieved [79]. Nanofibers of poly (ethyl 2-cyanoacrylate) were produced from stable macro-zwitterions of poly



(ethyl 2-cyanoacrylate). Macro-zwitterions of poly (ethyl 2-cyanoacrylate) were produced by zwitterionic polymerization of ethyl 2-cyanoacrylate monomer in presence of dimethyl sulfoxide resulting in macro-zwitterions [79]. Electrospun fibers formed from these macro-zwitterions of poly (ethyl 2-cyanoacrylate) were then thermally transformed into transparent textured coatings. These coatings show good scratch resistance, good biocompatibility, low friction coefficient, durability and self-cleaning properties [79].

## 4 Summary

Cyanoacrylate adhesives have been a fascinating material since their invention in 1950s. Cyanoacrylate adhesives have been established as a benchmark for a wide variety of commercial applications, including industrial, consumer and some of the medical applications for several decades due to their instant reactivity to form strong bonds with a variety of surfaces (both low and high energy surfaces) in the presence of moisture. The future prospects of cyanoacrylates lie in two key areas. First in the medical applications, with less toxic, longer shelf-life cyanoacrylate materials for internal tissue and surgical applications; and second area in structuring cyanoacrylate adhesives in the form of nanofibers. More developments leading to an economical and commercially scalable synthesis and production of these new cyanoacrylate based nanofibers can further expand the current application space into biomedical devices, self-cleaning polymer surfaces, coatings, electronics, filtration, etc. Cyanoacrylate adhesives have proven to find their niche through different enthralling applications/market sectors for several decades, and will surely continue to be more relevant in coming decades.

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